Rate and pathways for the reaction of OH with the biogenic p-cymene, an alkylated aromatic
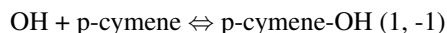
R. Strekowski (1), M.-T. Rayez (2), J.-C. Rayez (2), C. Zetzsch (3,4)

(1) Laboratoire Chimie Provence, Université de Provence, Marseille, France, (2) Institut des Science Moleculaires, Université Bordeaux 1, Talence, France, (3) Forschungsstelle für Atmosphärische Chemie, Universität Bayreuth, Germany (cornelius.zetzsch@bayceer.uni-bayreuth.de, +49-921-555729), (4) Fraunhofer-Institut für Toxikologie und Experimentelle Medizin, Hannover, Germany
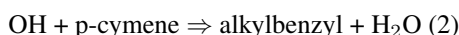
Aromatics are known to contribute strongly to tropospheric formation of ozone, and p-cymene (4-isopropyltoluene) is one of only a few biogenic, volatile aromatic hydrocarbons. In spite of its symmetry, this molecule ($CH_3 - \phi - CH(CH_3)_2$) has a multitude of potential pathways of its reaction with OH radicals. Addition of OH is well-known to be the predominating primary step in the tropospheric transformation of aromatic hydrocarbons. The addition is expected to occur preferably at a non-occupied position, where four positions are available: two equivalent ones ortho to the methyl group and two equivalent ones ortho to the isopropyl group. Furthermore, various C-H bonds (4 aromatic and 10 aliphatic) are available for abstraction, leading to benzyl-type radicals in two cases.

The present study combines theoretical calculations with kinetic experiments in the gas phase. The theoretical calculations are based on electronic quantum chemistry DFT method for the investigation of the possible pathways in the potential energy surface of the reaction. The experiments are carried out by the flash photolysis/resonance fluorescence technique.

OH radicals are produced by pulsed vacuum-UV photolysis of H_2O (> 115 nm) in the presence of p-cymene in a slow flow of He as carrier gas. Their pseudo-first-order decays are monitored by resonance fluorescence, storing the photon counts by multichannel scaling in a PC and accumulating 50 decays each; see Koch et al. (2007) for details of the technique and evaluation of data. The temperature was varied between room temperature (295 K) and 345K, the He pressure was 250 mbar, and the level of p-cymene was increased stepwise, up to 3 x 10^{13} molecules/cm^3. The decays of OH were observed to be exponential at room temperature, becoming clearly biexponential at higher temperatures, thus indicating reversible addition of OH according to the equilibration

$$OH + \text{p-cymene} \Leftrightarrow \text{p-cymene-OH} \quad (1, -1)$$

These reactions might be accompanied by various abstraction channels, summarized as

$$OH + \text{p-cymene} \Rightarrow \text{alkylbenzyl} + H_2O \quad (2)$$

A value of 1.4 x 10^{-11} cm^3 s^{-1} at 295 K is obtained for the sum $k_1 + k_2$, in good agreement with a value of 1.51 x 10^{-11} cm^3 s^{-1} determined by Corchnoy and Atkinson (1990) in a smog chamber at 295 K. The sum $k_1 + k_2$ decreases slightly with increasing temperature, falling below 10^{-11} cm^3 s^{-1} at 345 K. The Arrhenius plot reveals a curved behaviour with a negative activation energy, approximately 1 x 10^{-12} exp (60 K/T) cm^3 s^{-1}. The biexponential behaviour corresponds to an apparent equilibrium constant of k_1/k_{-1} = 8 x 10^{-25} exp [(-8500 ± 400) K/T] cm^3 s^{-1}. On the other hand, the bond energy of OH in the adduct can hardly be obtained from this biexponential behaviour alone since the abstraction of H atoms from the alkyl groups of p-cymene can be estimated to contribute markedly. Extrapolating the respective abstraction channels of toluene and the xylenes to two methyl substituents would yield k_2= 1.6 x 10^{-18} T^{2}exp (-38 K/T) cm^3 s^{-1} (Atkinson, 1989). This amounts to 1.2x10^{-12} cm^3 s^{-1} at 295 K (about 9% of the observed reactivity) and 1.7x10^{-12} cm^3 s^{-1} at 345K (>17% of the observed reactivity) and does not even take the possibly larger reactivity of the isopropyl group (as compared to CH_3) into account.

The abstraction channel has been found to predominate in the analogous reaction of atomic Cl with p-cymene (Finlayson-Pitts et al, 1999), and further experiments by other methods are required to clarify the reaction channels for OH radicals.

References

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